Abstract No. Piao0492

The Reaction of 1-chloro-2-methyl-2-propanol on Oxygen-covered Ag(110): C-Cl Bond Cleavage Behaviour for Epoxide Formation

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Beamline(s): U12A

Introduction: The understanding of the mechanism of silver-catalyzed olefin epoxidation has been the subject of both surface science and catalytic studies not only because of the industrial importance of this process, but also because the elucidation of the mechanism can shed light on similarities and differences between homogeneous and heterogeneous oxidation processes.

Methods and Materials: An oxygen-covered Ag(110) surface was investigated for the reaction using Soft X-ray photoelectron spectroscopy (XPS) in a UHV chamber on the U12A beamline at Brookhaven National Laboratory. The XPS spectra were collected in the fixed pass energy mode using a concentric hemispherical analyzer. With two sets of the gratings at 300 and 800 lines/mm as well as the availability of various photon energies, the energy resolution better than 0.3 eV can be obtained. Temperature Programmed XPS (TPXPS) and Temperature Programmed Desorption (TPD) data were collected using a heating rate of ~1 $K \cdot sec^{-1}$.

Results: An effort has been devoted to explore the C-Cl scission behaviour for the reaction of 1-chloro-2-methyl-2-propanol (Cl-*tert*-BuOH) on oxygen-covered Ag(110) surface. The C-Cl bond cleavage is one of the key steps to produce isobutene oxide (IBO) because it appears to be involved in the rate-determining step for the evolution of IBO [1]. However, the C-Cl bond cleavage mechanism was not fully understood. This motivated the surface reaction mechanism study to determine whether the surface chlorohydrin reaction follows an S_N1 (C-Cl bond breakage occurs before the IBO desorption begins from the surface) or S_N2 (they occur concurrently) path. Fig. 1 shows the evolution of the Cl2p spectra under various annealing temperatures for the surface with oxygen pre-coverage at 0.3 ML. As can be seen, the C-Cl bond cleavage has occurred at 250 K. In order to precisely determine the temperature window for C-Cl bond cleavage under various oxygen pre-coverages, the Temperature Programmed XPS (TPXPS) experiments were performed by tracing the changes of the $Cl2p_{3/2}$ signals for both chemisorbed Cl-*tert*-BuOH (200.6 $\pm$ 0.1 eV) and silver chloride (198.1 $\pm$ 0.1 eV) as a function of annealing temperature. With the help of the TPXPS, we have successfully located the temperature window in which C-Cl scission occurs (Fig. 2). With a comparison to the temperature window for IBO desorption obtained through TPD (Fig. 3), it has helped us to develop a fundamental understanding of the important role of the C-Cl bond cleavage in the surface chlorohydrin reaction.

Acknowledgments: This study was supported by the Seed Catalyst Project funded by BNL and the U.S. Department of Energy, Basic Energy Sciences. Dr. Mullins is gratefully thanked for his technical support as well as for the useful discussions about the results.

References:

[1] J.W. Medlin, M.A. Barteau, “The Reaction of 1-Chloro-2-methyl-2-propanol on Oxygen-covered Ag(11): Epoxide Formation via a Surface Chlorohydrin Reaction” , Surf. Sci. **506**, 105 (2002).

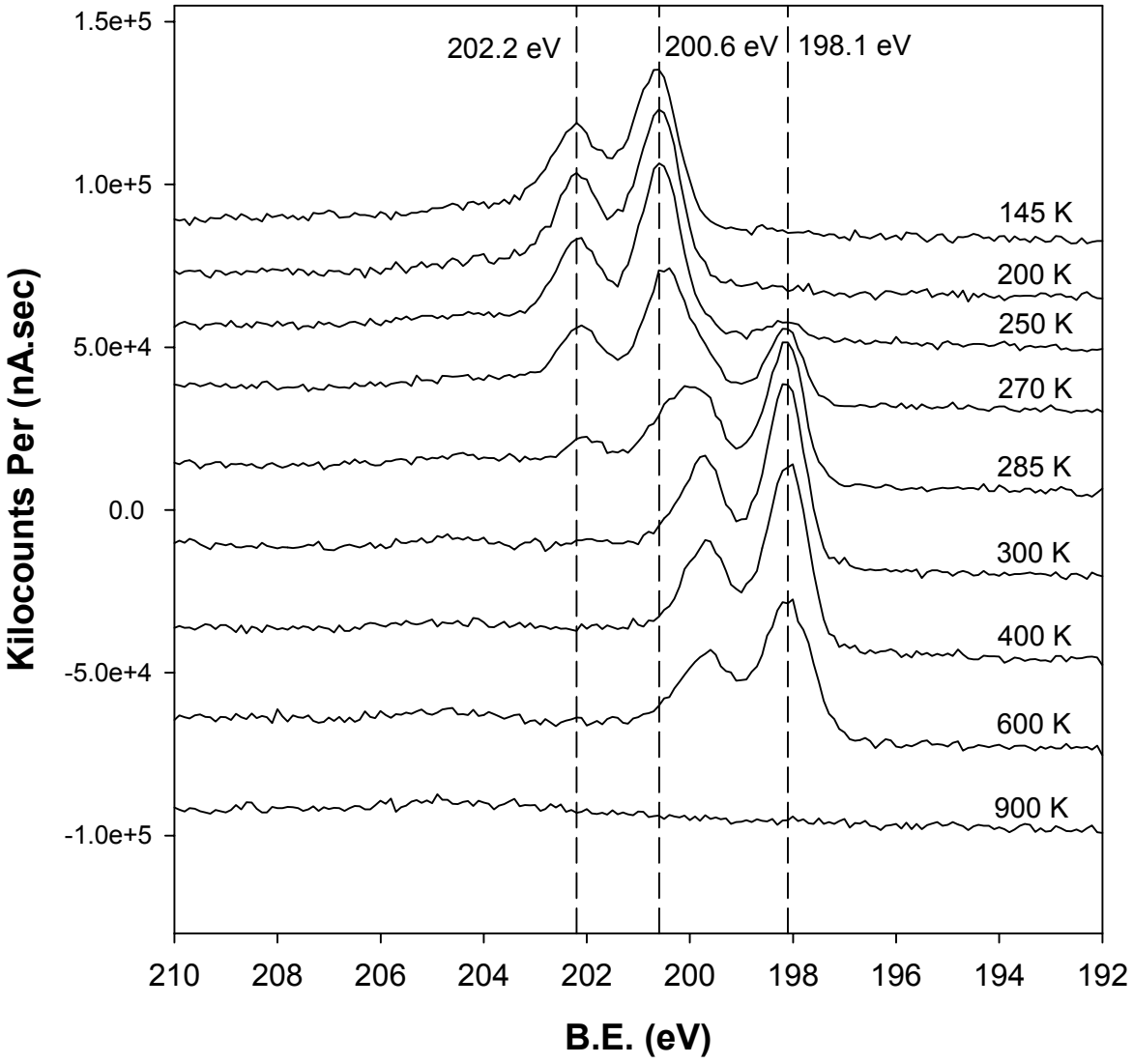

Fig. 1. The evolution of Cl2p spectra under various annealing temperatures for a saturation exposure of Cl-*tert*-BuOH on a 0.3 ML O-covered surface.

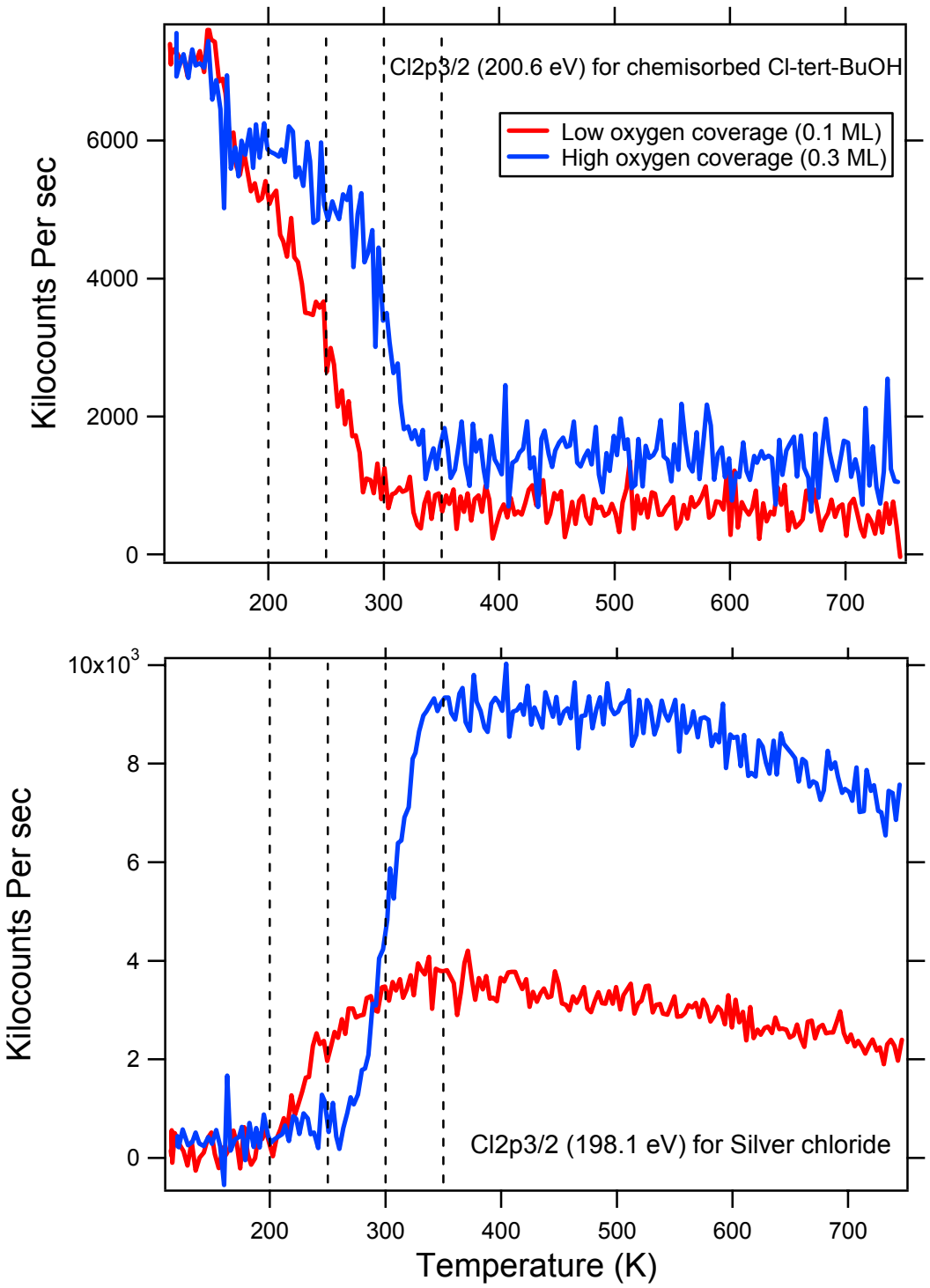

Fig. 2. Variations of intensitites of Cl2p3/2 lines for both chemisorbed Cl-t-BuOH and silver chloride species as a function of annealing temperature

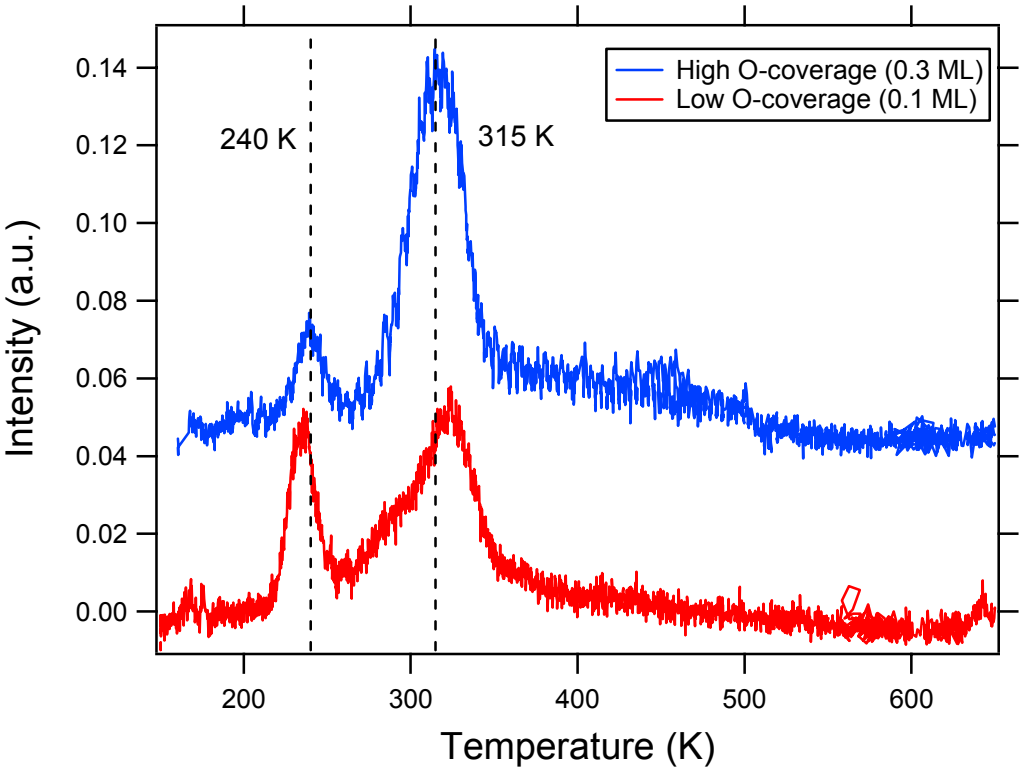

Fig. 3. Temperature-programmed desorption spectra of IBO (m/e = 41) after a saturation exposure of Cl-t-BuOH.